

1D exciton band and exciton-phonon interaction in a single polymer chain

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The excitonic luminescence of an isolated polydiacetylene polymer chain in its monomer matrix is studied by micro-photoluminescence. These chains behave as perfect 1D excitonic systems with the expected $1/\sqrt{E}$ density of states between 5 and 50 K. The temperature dependence of the homogeneous width is quantitatively explained by interaction with longitudinal acoustic phonons of the crystal in the range of temperature explored.

Conjugated polymers contain delocalized π electrons from conjugated unsaturated C-C bonds. They behave as organic semiconductors with large gap. They are usually highly disordered samples [1], but making use of the special polymerization mechanism of polydiacetylenes (PDAs) [2] a model system has been obtained in order to study the electronic properties of conjugated polymers. Diacetylenes are polymerized in the solid crystalline phase and by a judicious choice of side groups [2] and polymerization conditions, and one can obtain a monomer single crystal containing a very low concentration of chains of the corresponding PDA. These chains are highly ordered, non interacting, linear and very long [3]. These PDAs are organic large gap semiconductors where the principal electronic excitation is an exciton having most of the oscillator strength and a large binding energy of 0.5 eV [4]. Bulk PDAs are known to exist in two electronic structures called "red" and "blue" phases [5, 6] with an intense excitonic absorption around 2.4 and 2 eV respectively. In 3BCMU [2] monomer crystals both types of chains coexist and exhibit an excitonic resonance fluorescence [7]. Blue chain fluorescence is very weak whereas red chains have a high fluorescence quantum yield of 0.3 at 15 K [8]. The present work is exclusively concerned with red chains. The luminescence spectrum of red chains exhibits an intense zero phonon line and several

FIG. 1: Fluorescence emission spectrum of an ensemble of isolated red chains excited at 502 nm at 15 K. Full circles: zero phonon line at 2.28 eV. Open circles: vibronic emission spectrum; the two most intense vibronic lines correspond to the C=C stretch (D line at 2.09 eV) and C≡C stretch (T line at 2.015 eV) (From [10])

much weaker vibronic replicas (see Figure 1). The zero phonon line is centered at 2.28 eV at low temperature. The two main vibronic peaks correspond to the stretching of the C=C and C≡C bonds and will now be denoted by D and T respectively. These two lines are centered at 2.09 and 2.01 eV and are due to radiative recombination with emission of a chain optical phonon of the appropriate momentum [7].

The very high dilution of red chains and their high fluorescence yield allow the study of a single red chain by micro-photoluminescence (μ -PL) experiments [9]. The zero phonon line-shape is Lorentzian and much broader than calculated from the exciton lifetime [10]. The vibronic emission lines are broader and asymmetric. These line-shapes are analyzed below. It is shown that a purely 1D exciton density of states (DOS), i.e with its $1/\sqrt{E}$ singularity, quantitatively accounts for the vibronic line-shapes. This analysis requires the excitons to be in thermal equilibrium with the surrounding 3D monomer crystal lattice. Indeed, the temperature dependence of the zero phonon line-width is quantitatively explained by a 1D exciton-3D LA phonon interaction strong enough to ensure that thermal equilibrium.

The 3BCMU crystals analyzed were identical to the ones described in [9], i.e with a concentration of red chains smaller than 10^{-8} in weight. The excitation wavelength of the Ar^+ laser was chosen at 497 nm, nearly resonant to one vibronic absorption line. The excitation power was below $1 \mu W$ to keep the measurement in the low excitation regime, i.e with at most one exciton per chain. The excitation laser beam was focused on the sample

using a microscope objective with a numerical aperture of 0.6 yielding a diffraction limited laser spot of $\approx 1 \mu\text{m}$ diameter. The signal was analyzed through an imaging spectrometer coupled to a N_2 cooled CCD camera. The spectral resolution was about $100 \mu\text{eV}$.

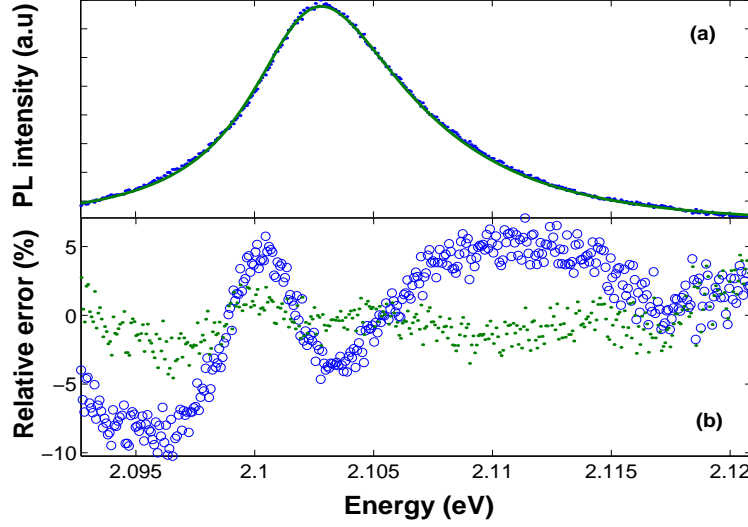


FIG. 2: (a) Data and fit using a 1D DOS of the D peak centered at 2.102 eV for $T=43$ K. (b) Comparison of the error (relative to the maximum signal value) between the fit function and the data for the 1D model (points) and for the 2D model (open circles). (From [11])

The D emission line at $T=43$ K is shown in Fig.2a. The line-shape is clearly non lorentzian, this emission can then not be that of a single state. In such a vibronic emission, the final state involves a 1D optical phonon of the chain so that any \mathbf{k} state of the exciton band is connected to the ground state by an optically allowed transition with generation of an optical phonon with the same \mathbf{k} . In Fig.2a, a fit barely distinguishable from the experimental data is presented as well, and the corresponding error is given in Fig.2b. This fit has been obtained considering that the energy dispersion of the optical phonons generated in the vibronic emissions is very small compared to the one of the excitons and is neglected. Since the effective mass of the exciton is found to be $\approx 0.3 m_0$ [10] (m_0 is the bare mass of the electron), this hypothesis seems very reasonable. Moreover the transition matrix elements between all the initial \mathbf{k} exciton states and the final state (emission of one photon and one chain optical phonon) are assumed equal (including the $\mathbf{k}=0$ state): the contribution of the initial \mathbf{k} state to the overall homogeneous width is the same for all \mathbf{k} .

The fitting function $f(E)$ is the convolution of the homogeneous lorentzian profile and the

population of emitting states (Eq.(1)). This population is the product of the DOS by the occupation probability. In (1) E_0 is the lorentzian's center position and Γ_{vib} its half width. A is a constant including the amplitude of the lorentzian and the constant parameters of the DOS. The only relevant parameter in the fitting routine is Γ_{vib} .

$$f(E) = \frac{A}{(E - E_0)^2 + \Gamma_{vib}^2} \star \left(\exp\left(-\frac{E - E_0}{k_B T}\right) \cdot DOS \right) \quad (1)$$

A quantitative 1D fit, i.e with a $(E - E_0)^{-1/2}$ DOS, is obtained for all vibronic lines at all temperature studied (5-50 K). Fitting with a 2D DOS is always worse. The 2D DOS corresponds to the lowest dimensionality non singular density of states. The fitting error for the 1D and 2D model are presented in Fig.2b, and show the very good accuracy of our model when a 1D DOS is used.

The analysis of the zero phonon emission line-width and its temperature dependence ($\Gamma_0(T)$) allow the study of the exciton-phonon interaction process. At low exciton densities and low temperature the exciton-phonon scattering process is dominated by acoustic phonons in semiconductors [12]. Then, to account for the thermal broadening of Γ_0 , we have studied the interaction between the 1D excitons confined on the polymer chain and acoustic phonons. Previous calculations made by Oh and Singh [13] for quantum wells have been adapted to the 1D polymer chain. According to [13], since 3BCMUs are a centro-symmetric crystal, the interaction with LA phonons is the only one to be considered. Furthermore, 1D exciton scattering by 1D LA phonon can just connect $\mathbf{k}=0$ to k_{1D} (k_{1D} is the solution of Eq.(9)). This is not in agreement with the experimental observation that all \mathbf{k} states emit within an energy range $k_B T$. Thus, we have considered exciton interactions with the 3D LA phonons of the monomer crystal.

This interaction derives from the deformation potential, and in second quantization the resulting Hamiltonian in one dimension is given by Eq.(2). K_x is the exciton momentum along the chain axis and y,z denote the confined directions of chain.

$$H_{ex-ph}(\vec{q}) = \sum_{K_x} C_D [F^-(\vec{q}) B_{K_x+q_x}^+ B_{K_x} b_{q_x} + F^+(\vec{q}) B_{K_x-q_x}^+ B_{K_x} b_{q_x}^+] \quad (2)$$

$$F^-(\vec{q}) = i[D_c(q)u_e(q_z)u_e(q_y)G(\alpha_h q_x) - D_v(q)u_h(q_z)u_h(q_y)G(-\alpha_e q_x)] \quad (3)$$

In (2) $B_{K_x}^+$ (B_{K_x}) are the creation (annihilation) operators of an exciton confined on the polymer chain with a wave vector K_x . $b_{q_x}^+$ (b_{q_x}) are the creation (annihilation) operators of

an LA phonon with momentum q_x along the chain. $C_D = \sqrt{\frac{\hbar q}{2\rho v_s V}}$ where V is the crystal volume, ρ the material density, q the modulus of the phonon momentum and v_s the sound velocity. $\vec{q} = (q_x, q_y, q_z)$ is the phonon wave vector, and the subscripts $+$ and $-$ denote phonon absorption and emission processes respectively. The exciton form factor F^- (note that $F^- = F^+$) is given by Eq. (3) where $\alpha_{h,e} = \frac{m_{h,e}}{m_X}$ (with $m_{e,h,X}$ the electron, hole, exciton effective mass). u_e (u_h) are the form factors of the electron (hole) of the exciton along the confined directions of the chain (Eq. (4)), and G_e (G_h) their form factors along the chain axis (Eq.(5)).

$$u_i(q_j) = \int dj_i |\phi_i(j_i)|^2 e^{iq_j j_i}; i = e, h : j = y, z \quad (4)$$

$$G(\alpha q_x) = \int dx e^{iq_x x} |\phi_X(x)|^2 \quad (5)$$

ϕ_e and ϕ_h are the electron and hole wave function for the lowest bound state for the charge carrier motion along the confined axis of the polymer chain. ϕ_X is the exciton wave function relative to its center of mass for the 1s state along the chain axis x . $D_c(q)$ and $D_v(q)$ are the deformation potential of the conduction and valence band respectively.

Finally, to quantify the thermal broadening of Γ_0 , the expression of the rate of a transition from $\mathbf{k}=0$ involving one LA phonon is obtained by applying the Fermi Golden rule. We note $|i\rangle$ and $|f\rangle$ the excitonic initial and final states. The transition matrix element is given in Eq.(6).

$$M(K_x \rightarrow K_x + q_x) = \langle f | H_{ex-ph}(\vec{q}) | i \rangle = C_D^2 |F^+|^2 f_{K_x}^X (f_{K_x+q_x}^X + 1) n_q \quad (6)$$

n_q is the occupation number of a phonon with momentum q , and f_K^X is the occupation number of an exciton with momentum K . The total rate for the transition from K_x is given by:

$$W(K_x) = \frac{2\pi}{\hbar} \sum_{q_x} |M(K_x \rightarrow K_x + q_x)|^2 \delta(E(K_x + q_x) - E(K_x) - \hbar v_s q) \quad (7)$$

The δ function in Eq.(7) induces a threshold in the scattering due to the 1D character of the excitons. The existence of this threshold does not depend on the dimensionality of the phonons involved in the scattering. This scattering process can be attributed to 1D LA

phonons confined on the chain or 3D LA phonons of the monomer. The argument of the delta function is given by Eq.(8) for 3D phonons and by Eq.(9) for 1D phonons.

$$E(K_x + q_x) - E(K_x) - \hbar v_s q = \frac{\hbar^2 q_x^2}{2m_X^*} - \hbar v_{s,3D} \sqrt{q_x^2 + q_y^2 + q_z^2} \quad (8)$$

$$E(K_x + q_x) - E(K_x) - \hbar v_s q = \frac{\hbar^2 q_x^2}{2m_X^*} - \hbar v_{s,1D} q_x \quad (9)$$

$v_{s,1D}$ is the sound velocity along the chain and $v_{s,3D}$ the one in the DA 3BCMU monomer matrix assumed isotropic. In the calculation the values measured in another (poly-)diacetylene, (poly-)pTS [14, 16] were used: $v_{s,1D} = 5.5 \cdot 10^3 \text{ m.s}^{-1}$ and $v_{s,3D} = 2.5 \cdot 10^3 \text{ m.s}^{-1}$ (the latter is typical for molecular crystals). The difference between them is due to the fact that the polymer is a chain of covalent bonds. As mentioned above, from Eq.(9) one remarks that exciton scattering by 1D LA phonon can just connect $\mathbf{k}=0$ to k_{1D} . On the contrary scattering by 3D LA phonons of the monomer matrix can connect $\mathbf{k}=0$ to a continuum of states with $\mathbf{k} > \mathbf{k}_{3D}^{min}$. With $m_X^* = 0.3 m_0$ [10] one finds $\mathbf{k}_{3D}^{min} = 8.2 \cdot 10^{-4} \text{ \AA}^{-1}$. We also want to note that in Eq.(8) the 3D LA phonon dispersion curve is considered linear which is a reasonable approximation since the \mathbf{q} phonon states which contribute significantly to the scattering are within the first tenth of the first Brillouin zone. The variation of the transition rate is not highly dependent on the exciton Bohr radius which is between 10 and 20 \AA [4, 15] (see Fig. 3). An exciton effective mass $m_X^* = (0.3 \pm 0.1) m_0$ [10] leads to typical deformation potential values of $(D_c + D_v) = 6.1 \mp 0.8 \text{ eV}$. The calculated scattering rate goes to zero at 0 K so a constant parameter has been added in order to reproduce experimental data. Its fitted value of 150 μeV is much larger than the contribution of the effective lifetime of the exciton at 1 K (approximately 6 μeV) [10]. This cannot be only due to instrumental resolution and will be the subject of further analysis.

Thus, as shown in Figure 3 exciton scattering by 3D LA phonons of the monomer matrix quantitatively explains the thermal broadening of Γ_0 . This thermalization process has a characteristic time of 2 ps or less (see the widths in Fig. 3). Since the excitons have effective lifetimes over 100 ps in the range of temperatures studied [10], excitons of the chain are in thermodynamic equilibrium with the surrounding medium.

To summarize, we have presented micro-fluorescence experiments performed on a single conjugated polymer chain in a crystalline matrix. The zero phonon emission line is lorentzian while the vibronic ones are asymmetric. Fitting the line-shape of these vibronic peaks shows

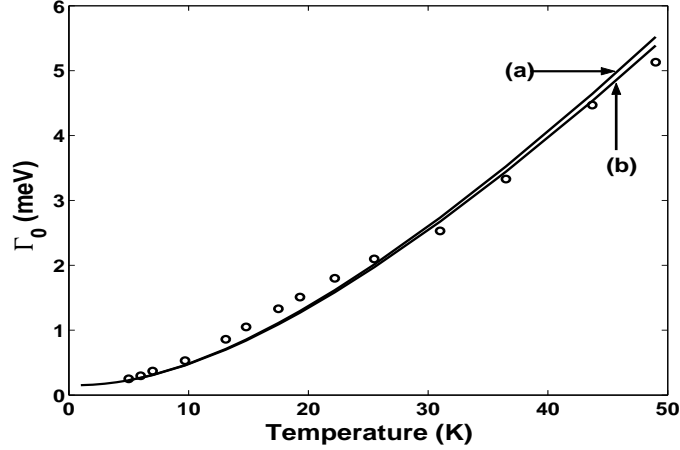


FIG. 3: Experimental data (open circles) and calculated variation of Γ_0 with temperature, for an exciton Bohr radius of 10 and 20 Å ((a) and (b) respectively) and an effective mass of $0.3 m_0$. In both cases, the sum of the deformation potential for the valence and conduction band is ≈ 6 eV.

that the chain is a one dimensional system which has to be described by an excitonic band with a $1/\sqrt{E}$ DOS. Furthermore, the variation of Γ_0 with temperature is explained by interactions with longitudinal acoustic phonons of the 3D surrounding crystal in the range of temperatures studied. This interaction thermalizes the excitons in their band so that they are at thermodynamic equilibrium with the surrounding medium.

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[1] M. Schott, in Organic Conductors fundamentals and applications, Ed. by J-P. Farges, Marcel Dekker, 539 (1994)

[2] The general formula of PDA is $(=CR-C\equiv C-CR'=)_n$. R and R' can be a large variety of chemical groups. In 3BCMU, R and R' are identical with the following molecular formula: $-(CH_2)_3OCONHCH_2COOC_4H_9$

- [3] S. Spagnoli, J. Berréhar, C. Lapersonne-Meyer, M. Schott, A Rameau, and M. Rawiso, *Macromolecules* **29**, 5615 (1996)
- [4] A. Horvath, G. Weiser, C. Lapersonne-Meyer, M. Schott, and S. Spagnoli, *Phys. Rev. B.* **53**, 13507 (1996)
- [5] H. Eckhardt, C. Eckhardt, and K. Lee, *J. Chem. Phys.* **70**, 5498 (1979)
- [6] S. Koshihara, Y. Tokura, K. Takeda, T. Koda, and A. Kobayashi, *J. Chem. Phys.* **92**, 7581 (1990)
- [7] R. Lécuiller, J. Berréhar, C. Lapersonne-Meyer, and M. Schott, *Phys. Rev. Lett.* **80**, 4068 (1998)
- [8] R. Lécuiller, J. Berréhar, C. Lapersonne-Meyer, M. Schott, and J.-D. Ganière, *Chem. Phys. Lett.* **314**, 255 (1999)
- [9] T. Guillet, J. Berréhar, R. Grousson, J. Kovensky, C. Lapersonne-Meyer, M. Schott and V. Voliotis, *Phys. Rev. Lett.* **87**, 087401 (2001)
- [10] R. Lécuiller, J. Berréhar, J.-D. Ganière, C. Lapersonne-Meyer, P. Lavallard, and M. Schott, to be published.
- [11] F. Dubin, J. Berréhar, R. Grousson, T. Guillet, C. Lapersonne-Meyer, M. Schott, and V. Voliotis, submitted to *Phys. Rev.*
- [12] P.K. Basu, and P. Ray, *Phys. Rev. B.* **45**, 1907 (1992)
- [13] I.-K. Oh, and Jai Singh, *Journal of Luminescence* **85**, 233 (2000)
- [14] W. Rehwald, A. Vonlanthen, and W. Meyer, *Phys. Stat. Sol. (a)*, **75**, 219 (1983)
- [15] S. Suhai, *Phys. Rev. B.* **29**, 4570 (1984)
- [16] R. J. Leyrer, G. Wegner, and W. Wettling, *Ber. Bunsenges. Phys. Chem.*, **82**, 697 (1978)